

UNCLASSIFIED

**Defense Technical Information Center  
Compilation Part Notice**

**ADP014225**

**TITLE:** Development of PZT Suspensions for Ceramic Ink-Jet Printing

**DISTRIBUTION:** Approved for public release, distribution unlimited

**This paper is part of the following report:**

**TITLE:** Materials Research Society Symposium Proceedings, Volume 758  
Held in Boston, Massachusetts on December 3-5, 2002. Rapid Prototyping  
Technologies

**To order the complete compilation report, use: ADA417756**

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:  
ADP014213 thru ADP014236

UNCLASSIFIED

## Development of PZT Suspensions for Ceramic Ink-Jet Printing

B. Derby, D.H. Lee, T. Wang and D. Hall

Manchester Materials Science Centre, UMIST and the University of Manchester,  
Grosvenor St., Manchester, M1 7HS, UK

### ABSTRACT

The direct ink-jet printing of ceramic powders requires the development of highly fluid suspensions of ceramic particles with viscosity  $< 40$  mPas. Here we describe the development of two such ceramic suspensions, which contain up to 30% by volume of PZT particles in either an azeotropic mixture of MEK and ethanol or in an alkane wax at 120 °C. The influence of various processing parameters on fluid rheology are investigated and trial fluids have been passed through an ink-jet printing head.

### INTRODUCTION

Ink-jet printing is now a mature technology and has widespread applications in the fields of printing, product marking and microdosing. Initial work combining ink-jet printing and layered manufacturing for the production of ceramic parts was undertaken by Sachs and co-workers, using a process of selectively printing binders onto powder beds [1]. Evans and co-workers extended this concept by pioneering the direct printing of ceramic suspensions using ink-jet printers [2-4]. Direct ink-jet printing is a very attractive route for the freeform fabrication of ceramics as fabrication of an object by droplet deposition allows the composition of each voxel of a design to be individually determined. This extends the fabrication method to components requiring multiple materials or materials of graded composition.

Initial studies of direct ink-jet printing used commercial ink-jet printers optimised for text printing, and thus the volume of ceramic powder available in suspension was relatively low ( $< 10$  volume%). This was because the viscosity of the suspensions had to be low to allow printing using the unmodified printers available. Evans' work used ceramic suspensions in aqueous or alcohol-based media. The liquid carrier or solvent is removed by evaporation from the deposit after printing. Solid objects can be fabricated by overprinting, however the combination of low solid volume, and the need to remove the solvent before deposition of subsequent layers, resulted in a relatively low rate of growth in the direction normal to the printed plane.

Our earlier work on ceramic ink-jet printing used alumina powders suspended in low melting point alkane (paraffin) waxes [5,6]. These suspensions solidify on impact and build up a thickness more rapidly than do deposits that solidify by evaporation. Both these methods have their advantages and disadvantages. Suspending fluids that evaporate allow dilute, low viscosity ceramic particle suspensions to be used. However solid distribution during drying is affected by Marangoni convection and the resulting deposit may show an irregular packing density. Phase-change fluids that solidify on impact result in more uniform particle distributions but now the solidified fluid must be removed from the object by an additional processing step prior to firing. Whichever route is used to prepare printable fluids, it is desirable to obtain the maximum fraction of particles in stable suspension while maintaining a fluid viscosity sufficiently low to allow droplet formation in an ink-jet printing device. Using the ink-jet printing systems available at

Manchester this viscosity limit is 40 mPas at the printing temperature. With alumina powders it is possible to achieve stable suspensions with up to 40% solids fraction with viscosity sufficiently low for ink-jet printing [6].

In this article we describe methods to produce printable suspensions of the piezoelectric ceramic lead ziconate titanate (PZT) in wax and other solvents.

## MATERIALS AND EXPERIMENTAL PROCEDURE

PZT powder, of grade PC5H (a soft piezoelectric material), was provided by Morgan Electroceramics (Wrexham, UK). Two solvent systems have been investigated using either a paraffin (alkane) wax of melting temperature 57 °C (Aldrich, Poole, UK) or an azeotropic mixture of 67% methyl ethyl ketone and 33% absolute ethanol (MEK/EtOH) (Aldrich, Poole, UK). Two dispersant systems have been used: a commercial polyester dispersant (Hypermer LP1, Uniqema, Everberg, Belgium) — combined with Octadecylamine (Aldrich, Poole, UK) and a phosphate ester based dispersant (Phospholan PE182, Akros Chemicals, Manchester, UK).

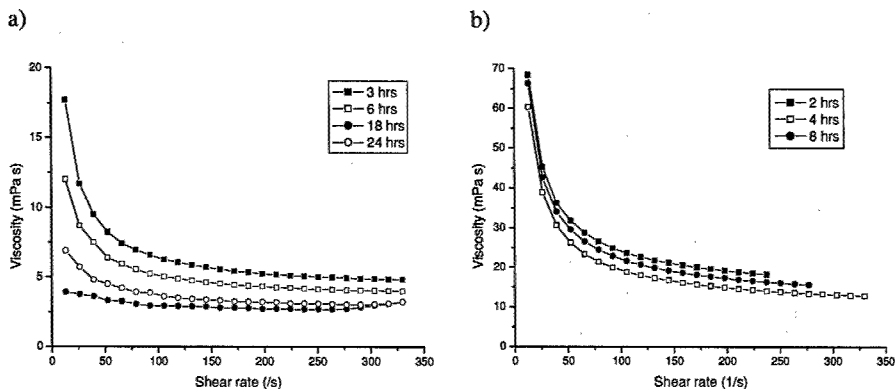
The PZT powder was calcined for 5 hours at 650 °C to remove a polymeric binder on the as-received powder. The calcined powder was either ball milled for 72 hours or attrition milled for 6 hours in alcohol to remove any agglomeration that occurred during calcining. The dried powders were mixed with the appropriate medium and dispersant before ball milling for up to 24 hours at 10 – 20 rpm. The mixing/milling process was conducted at room temperature with the MEK/EtOH solvent. The temperature of mixing for the wax-based suspension was 120 °C, which is the operating temperature of the high temperature ink jet head.

Suspension viscosity was measured using a concentric cylinder rheometer (Brookfield, Middleboro, MA, USA). Suspension stability was assessed by leaving suspensions in measuring cylinders at the appropriate temperature and investigating particle distribution after periods of time. In order to assess the printability of the suspensions they were passed through a single ink-jet printing head. For the MEK/EtOH solvent system a room temperature printhead was used (Microfab, Plano, TX, USA), while for the wax based system a system optimised for printing at 120°C was used (Sanders Design International, Wilton NH, USA).

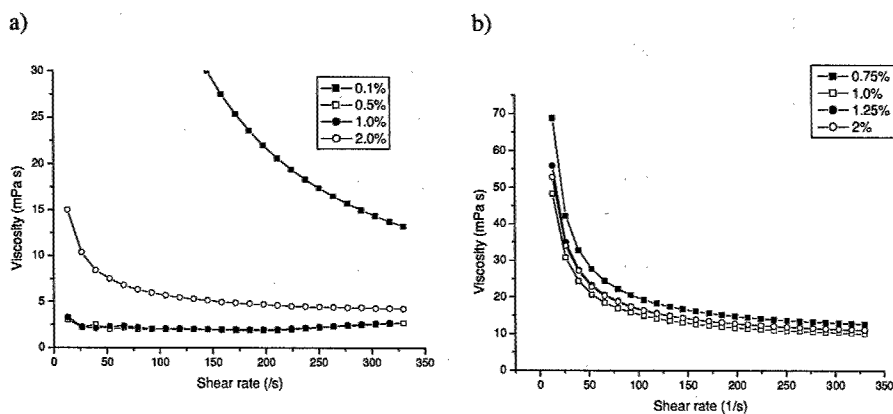
## RESULTS AND DISCUSSION

For the initial trials the phosphate ester dispersant system was used. This gave reasonably stable suspensions in both MEK/EtOH and wax solvents. Suspension viscosity was found to be strongly affected by ball milling with longer milling times giving lower viscosity up to some optimum time above which viscosity increased again. This increase in viscosity is believed to indicate the thermomechanical degradation of the dispersant molecules during milling. This behaviour is clearly seen in figure 1 where the optimum milling time for a 20% by volume dispersion of PZT in the MEK/EtOH solvent is 18 hours, and for the wax solvent 4 hours. The shorter time before degradation found with the wax-based materials is believed to be because this material is milled at 120 °C.

Suspension viscosity was also found to depend strongly on the amount of dispersant used. The behaviour in figure 2 also shows an optimum result at 1% by weight of the phosphate ester for both solvent media when 20 vol% PZT is in suspension. The optimum value indicates site saturation on the PZT particle surface. Any dispersant in addition to this value remains in solution and increases viscosity without further improving particle dispersion. Figure 3 shows the



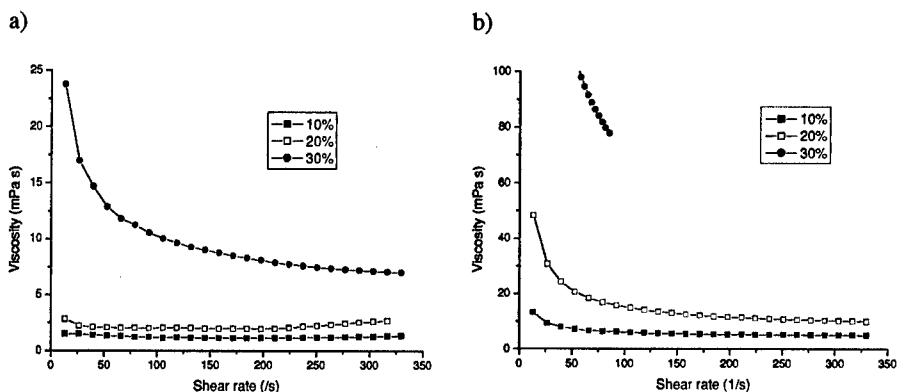
**Figure 1.** Viscosity of 20 vol% PZT suspensions, with 1 wt% PE182 dispersant, as a function of shear rate after various ball milling times: a) MEK/EtOH solvent at room temperature, b) wax solvent at 120 °C.



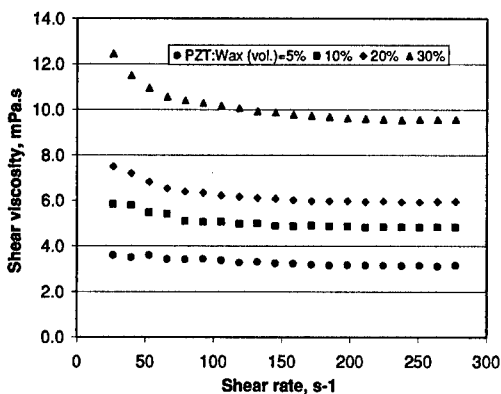
**Figure 2.** Effect of varying the content of phosphate ester dispersant on the viscosity of the 20 vol% PZT suspensions : a) MEK/EtOH solvent at room temperature, b) wax solvent at 120 °C.

effect of increasing particle volume in suspension. With the MEK/EtOH solvent the suspension viscosity is sufficiently low to allow printing at 30 vol% PZT. However, the viscosity of the wax based material is too high.

There are a number of potential applications for components fabricated from PZT where the higher aspect ratio deposit available through printing wax based suspensions would be an advantage. Hence a different dispersant system based on a commercial polyester was studied. Previous work on alumina had identified the Hypermer series of dispersants as being particularly effective with alumina [5,6] and these were explored for use with PZT.



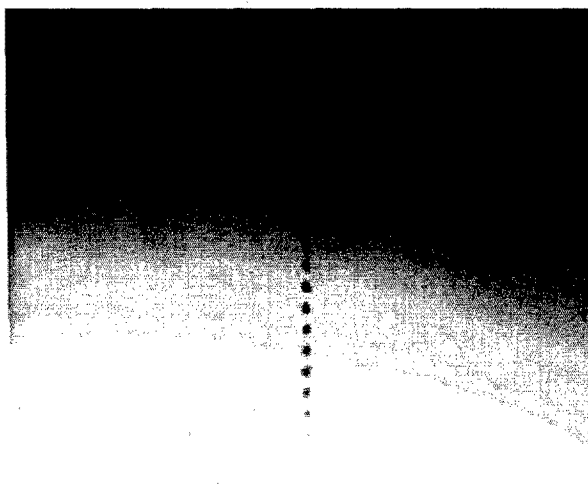
**Figure 3.** The influence of the volume fraction of PZT particles in suspension on fluid viscosity : a) MEK/EtOH solvent at room temperature, b) wax solvent at 120 °C.



**Figure 4.** Viscosity of PZT suspensions in wax as a function of volume solids, measured at 120 °C with Hypermer LP1 dispersant.

It is well known that a combination of long chain and short chain surfactant molecules can be particularly effective in dispersing ceramics particles [7]. Earlier work had shown that Hypermer LP1 can be used with octadecanoic acid (stearic acid) and octadecylamine to produce suspensions of alumina in wax with very low viscosity [5, 6]

Suspensions of PZT in wax were prepared containing 1 wt% Hypermer LP1 and 0.5 wt% octadecylamine and a range of PZT powder concentrations. These were ball milled for 6 hours at 120 °C to ensure adequate dispersion. The viscosity of this range of materials was measured and the results given in figure 4. On comparing figure 4 with figure 3b it is clear that the Hypermer LP1 dispersant system gives significantly lower viscosities than the phosphate ester system.



**Figure 5.** Ink-jet printed droplets of 30 vol% PZT suspension in MEK/EtOH.

Both the phosphate ester dispersed MEK/EtOH and the Hypermer dispersed wax based system have sufficiently low viscosity at 30 vol% PZT to be printable. Preliminary trials have been successful (figure 5) with the fluids having been successfully printed through the test station.

## CONCLUSIONS

It is possible to prepare PZT suspensions of high solid loading that can be successfully used for ink-jet printing. A phosphate ester dispersant has been used with MEK/EtOH azeotropic solvents while a combination of a polyester and a short chain amine terminated alkane produces the best result with wax as a solvent.

## ACKNOWLEDGEMENTS

We would like to acknowledge the support of the EPSRC and Ministry of Defence through project grant reference GR/N16969. We also acknowledge the support of Morgan Electroceramics who provided the PZT powder.

## REFERENCES

1. E. Sachs, M. Cima, P. Williams, D. Brancazio, and J. Cornie, *J. Eng. Industry - Trans. ASME* **114**, 481 (1992).
2. P. F. Blazdell and J. R. G. Evans, *J. Mater. Process. Tech.* **99**, 94 (2000).
3. C. E. Slade and J. R. G. Evans, *J. Mater. Sci. Lett.* **17**, 1669 (1998).

4. Q. F. Xiang, J. R. G. Evans, M. J. Edirisinghe, and P. F. Blazdell, *Proc. Inst. Mech. Eng. B – J. Eng. Manuf.* **211**, 211 (1997)
5. K. A. M. Seerden, N. Reis, J. R. G. Evans, P. S. Grant, J. W. Halloran, and B. Derby, *Journal of the American Ceramic Society*, **84**, (2001) 2514-2420.
6. C. Ainsley, N. Reis and B. Derby, *J. Mater. Sci.* **35**, 3155 (2002).
7. J.H. Song and J.R.G. Evans, *J. Rheol.* **40**, 131-152 (1996).